

Strength and porosity evolution of two cement mortar submerged in pig slurry

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Abstract

Pig slurry is an agricultural by-product used chiefly to fertilize cultivated fields. The demand for fertilizer depends on crop cycles. So, the slurry must be stored over long periods of time. In Spain, the lagoons of different depths generally used for such storage are made of brick covered with plain or reinforced concrete. Also, the slurry is in contact with other precast concrete structural members. The degradation of these structures may entail substantial economic loss, in patterned flooring especially, where deterioration-induced collapse can cause severe injury to the animals.

The paper presents two aspects related to the durability of the mortar cements. In it addresses the variations observed in porosity and flexural and compressive strength in two types of cement mortar when submerged in pig slurry. The tests were conducted in a 100 m³ experimental lagoon. The mortars were exposed to three types of environments for 36 months: one outside the test lagoon and two submerged in it, at two different depths. Bending and compression measurements were taken after 3, 12, 24 and 36 months. In addition, 3, 24 and 36 month specimens were tested for total porosity and pore-size distribution.

1. Introduction

Pig slurry is an agricultural by-product used chiefly to fertilize cultivated fields. The demand for fertilizer depends on crop cycles. So, the slurry must be stored over long periods of time. In Spain, the lagoons of different depths generally used for such storage are made of brick covered with plain or reinforced concrete. These lagoons are not watertight due to the appearance of cracks or leaks, with the concomitant risk of environmental damage in the form of the pollution of underground or runoff water [1]. In farm enclosures slurry is also in contact with other precast concrete structural members, such as continuous or patterned flooring. The degradation of these structures may entail substantial economic loss, in

patterned flooring especially, where deterioration-induced collapse can cause severe injury to the animals [2-3].

Slurry composition depends on many factors, including animal physiology, type of feed, facility typology and management and so forth. Its complex chemical composition, with organic and inorganic compounds, varied over time. The three main groups of organic components were: organic acid (acetic, propionic, isovaleric), nitrogenous compounds (primarily ammonia-based) and a number of hydrosulphide compounds deriving from urea denaturation. The result is a compound with a pH ranging from 7 to 8. The Spanish structural concrete code, EHE [4], regards substances with a pH of over 6.5 to be non-aggressive from the standpoint of acid damage. Nonetheless, research has shown that concrete and mortar in contact with such slurries deteriorate systematically, with a decline in their load capacity [5]. Clearly, then, degradation is the outcome of the synergies between various factors. Some researchers have attempted to reproduce this sort of concrete degradation in the laboratory [6], by testing different types of cements after exposure to specific organic salts with varying pH values or analyzing the mechanism involved in cement matrix alterations caused by a combination of acids [7].

The use of sulphate-resistant Portland cement and pozzolanic cements with silica fume or fly ash additions is standard practice in concrete farm buildings in a number of countries [3]. In Spain, the cements most commonly used in rural environments are type I Portland and Portland with additions, particularly fly ash. The use of the former is based on its availability and suitability for works of all kinds. The latter is used due to its lower cost, and the added advantage that replacing part of the Portland cement with fly ash improves mortar and concrete durability by enhancing resistance to chemical agents and reducing permeability [8-10].

This paper reports on research conducted to ascertain the impact of pig slurry on mortars made with different types of cement. The values found for flexural and compressive strength, total porosity and pore size distribution at different test times are given.

2. Materials and methods

2.1. Cements

The study was conducted with two types of cement: a sulphate-resistant Portland cement, CEM I SR 42.5 N, and a blended cement with fly ash and limestone filler, CEM II / B-M (V-L) 32.5 N. The chemical and mineralogical compositions of the two cements are given in Table 1.

Table 1. Chemical and mineralogical composition of the cements used

	Ca O	% CO libre	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	SO ₃	Cl	Na ₂ O	Loss on ignition
CEM I SR 42.5N	64.4	2.1	19.1	3.9	4.7	1.3	0.7	3.1	-	0.2	2.6
CEM II/B-M (V-L) 32.5N	51.36	-	24.80	9.19	3.25	2.14	1.41	2.58	0.006	-	1.75

Three prismatic specimens (40 x 40 x 160 cm) with a water/cement ratio of 0.5 and a sand/cement ratio of 3/1 were prepared for each cement type, environment and exposure time. The specimens were made to European standard EN 196-1:194 requirements. They were de-moulded 24 hours later and cured in water for 28 days at 22°C. Zero time tests were conducted on three samples of each mortar type, while the others were placed in the respective aggressive environments.

2.2. Aggressive medium

The aggressive medium used was pig slurry from a farm storage lagoon at Etreros in the Spanish province of Segovia.

The farm is located in central Spain, where the mean summertime relative humidity is 48% and the mean temperature is 20°C. The values for the rest of the year are 75% and 9°C, respectively. The area has 56 frost days per year.

The slurry composition is variable. It depend a many factors than changed along time. Therefore, the slurry was sampled and analyzed after 3, 6, 12, 18, 24 and 36 months. The minimum, maximum and mean values are shown in Table 2.

The highest content values were found for ammonia nitrogen, sulphides, chlorides and acetic and propionic acid. The maximum value of ammonia nitrogen present (0.25%), taking NH₄⁺ separately, was sufficiently high to classify the slurry as a medium or highly aggressive substance, according to Spanish structural concrete code EHE [4]. The maximum chloride content, whose origin is to be found in the cleaning water used to hose the facility, generated salinity similar to the values observed in seawater (1472 mg/l in aerobic, and 780 mg/l in anaerobic environments). Moreover, the acetic acid content was high enough to cause acid attack. Another potentially aggressive agent was the pH, which at values ranging from 7.21 to 8.13 was much lower than the mortar pore solution pH (12.7) [11]. Inasmuch as this pH gradient may lead to the dissolution of the much more basic portlandite, slurry can be regarded to be an aggressive substance.

Table 2. Slurry composition: minimum, maximum and average values

		Aerobic Environment			Anaerobic Environment		
		Min.	Aver.	Max.	Min.	Aver.	Max.
pH		7.30	7.67	8.10	7.21	7.52	8.13
Total nitrogen (%)		0.06	0.19	0.28	0.06	0.22	0.38
Ammoniac nitrogen (%)		0.05	0.10	0.12	0.05	0.13	0.25
Sulphurs (mg/l)		5.36	81.24	115.00	4.80	90.32	162.87
Bicarbonates (mg/l)		3.38	5.85	10.55	3.37	7.13	11.66
	Sulphurs (mg/l)	0.00	7.35	12.79	0.00	23.55	177.95
Anions	Chlorides (mg/l)	61.00	462.42	1427.00	209.00	445.83	780.00
	Acetic (mg/l)	32.55	153.79	286.70	7.86	89.13	192.00
	Propionic (mg/l)	0.00	48.96	124.60	0.00	27.85	93.890
Acids	Isovaleric (mg/l)	0.00	2.13	3.50	0.00	0.56	1.20

2.3. Experimental procedures

The tests were conducted in an experimental lagoon located near the farm's own storage lagoon. Its two basins measured 4x8 m with depths of one and three metres, inter-connected by a canal to facilitate the filling process. A detailed sketch of the experimental facility is given in E. Sánchez et al. [12].

The specimens were placed on the bottom of the basins, where conditions were aerobic at a depth of one and anaerobic at a depth of three metres. These conditions reproduced the environments prevailing on pig farms (lagoons from 1 to 1.5 m deep and tanks or deep lagoons 2 to 4 m deep). Control specimens were placed in the open air alongside the canal connecting the two basins. Consequently, three aggressive environments were studied:

- A natural environment (I) with full oxygen and carbon dioxide availability.
- An aerobic environment (II) in slurry one metre deep, with medium to low oxygen content and aerobic fermentation.
- An anaerobic environment (III) with specimens submerged in 3-m deep slurry, with zero oxygen and anaerobic fermentation.

Three specimens were withdrawn from each environment after 3, 12, 24 and 36 months, washed and submerged in water for 48 hours. Compressive and flexural strength tests were subsequently conducted to European standard EN196-1:1994 at INTEMAC's (Instituto Técnico de Materiales y Construcciones) central laboratory.

Mortar microstructure was characterized after 24 and 36 months of exposure to the aggressive medium.

Mercury intrusion porosity (MIP) trials were run on a Micromeritics Autopore IV 9500 porosimeter that operates at pressures of up to 33,000 psi (228 MPa) and covers pore diameters of from 175 to 0.006 μm . Each 3-g specimen was dried for 48 hours at a temperature of 22 ± 2 °C and a relative humidity of 50%. The samples were taken from one of the exposed sides of the specimen and tested after reaching a constant weight, to an accuracy of 0.01 g. Sample weight was stabilized in an oven at 40 °C.

3. Results and discussion

3.1. Mechanical strength

An ANOVA was run on the strength values. This entailed, for both compressive and flexural strength, verifying the normal distribution fitting of the residual values, finding the difference, for each data item in a given group, between that value and the mean value for the group. The analysis showed that there were no systematic errors attributable to measurements or specimen manufacture.

3.1.1. Flexural strength

Figures 1 and 2 show the flexural strength results in the three environments for mortars made with cements CEM I and CEM II. Performance was similar in the two cements, although with slight differences. In CEM I bending strength remained essentially unchanged up to 12 months in all three environments, with a slight rise in strength at 24 months and a decline after 36. CEM II performed nearly identically in the two submerged environments, but exhibited a steady decline in strength in the natural environment. In the natural environment, the flexural strength was similar in the two cements, with insignificant differences. Differences in flexural strength were found, however, between natural and submerged environment specimens. The values obtained for submerged specimens were significantly greater than the values for the samples exposed to a natural environment.

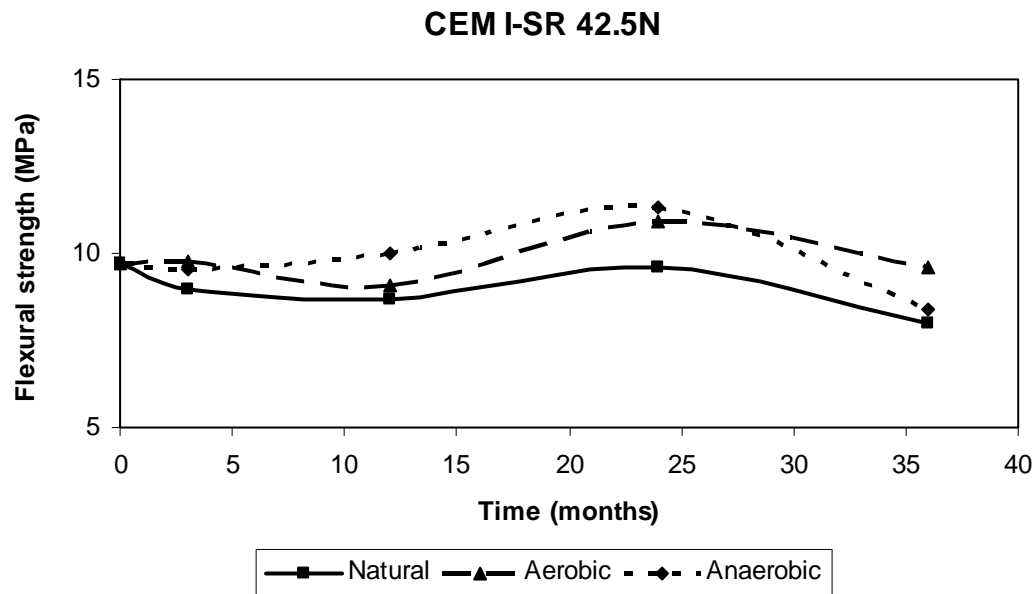


Figure 1. Variation of flexural strength for the CEM I in the three environments.

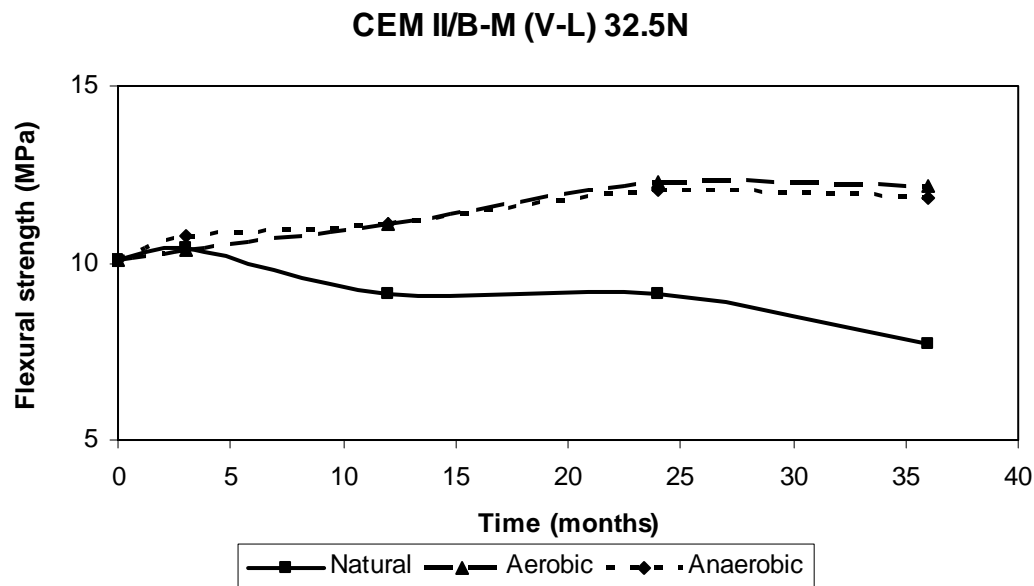


Figure 2. Variation of flexural strength for the CEM II in the three environments.

The two cements performed similar in both submerged environments. After 24 months the flexural strength values for the two cements differed by less than 2 MPa. After 36 months these differences increased to around 3 MPa. The decline in CEM I flexural strength between 24 and 36 months was 12% in the aerobic environment and 25% in the anaerobic environment. CEM II strength values did not differ significantly between 24 and 36 months. CEM II exhibited consistently higher flexural strength values than CEM I throughout the test,

despite its lower strength class (32.5 N compared to 42.5 N for CEM I). The authors believe that this is due to the increased hydration resulting from the fly ash-mediated pozzolanic reactions taking place in cement CEM II [10, 12-14].

3.1.2. Compressive strength

Figures 3 and 4 show the compressive strength findings for cements CEM I and CEM II in the three environments.

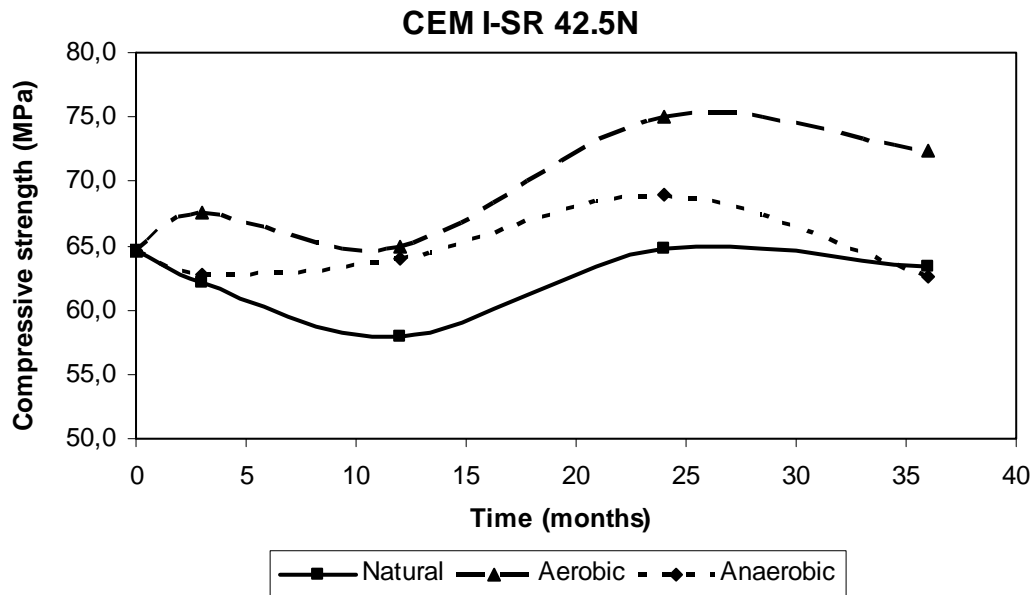


Figure 3. Variation of compressive strength for the CEM I in the three environments.

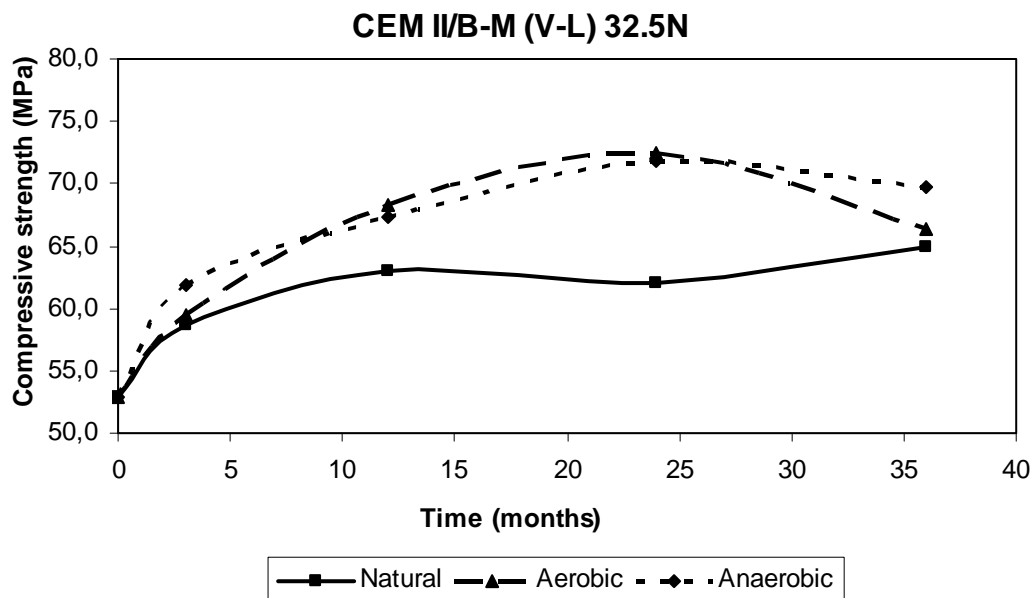


Figure 4. Variation of compressive strength for the CEM II in the three environments

In the natural environment, cement CEM I declined steadily by a total of 10% during the first 12 months of exposure. The initial value was recovered between 12 and 24 months, and then maintained up through the end of the trial (36 months). CEM II followed a pattern typical of Portland cement with fly ash additions, i.e., a steady increase of 17% in the first 12 months followed by a slight increase subsequently maintained through the end of the 36-month trial period [12-15].

In submerged environments, strength tended to increase in both cements up to 24 months, and decline after 36 months of exposure. In the aerobic environment, CEM I maintained its compressive strength with no significant variations up to the twelfth month of exposure, and showed an increase of around 16% after 24 months. This increase was 7% in the anaerobic environment. Strength declined in this cement after 36 months in both environments, by about 3.5% in the aerobic and 9.5% in the anaerobic medium.

No significant differences were recorded in cement CEM II performance in the two submerged environments, a finding that concurred with earlier results obtained by E. Sánchez et al. [12]. Strength increased steadily in this cement by a total of around 36% up to 24 months of exposure. The strength declined in both environments after 36 months, by about 8.5% and 3% in the aerobic and anaerobic media, respectively.

The increase in compressive strength in the natural environment was on the order of one half of the rise found in the submerged environments. After 36 months, however, strength values tended to converge, with no significant differences between the natural and aerobic environments.

Significant differences were found between the cements in the anaerobic environment, with CEM II exhibiting consistently higher strength than CEM I. In the aerobic environment, however, the CEM I values were significantly higher after both 24 and 36 months.

3.2. Porosity tests

Figure 5 shows the total porosity for the two cements studied at different test ages and in different environments. Porosity was observed to decline in all cases after 24 months of exposure. The greatest decline, at around 30%, was recorded for cement CEM I in the aerobic environment (I) and CEM II in the anaerobic environment (II). After 36 months, porosity generally tended upward. The highest rise, at around 20%, was found in the same environments and cements as cited above. Initial porosity was not attained in any of the cases.

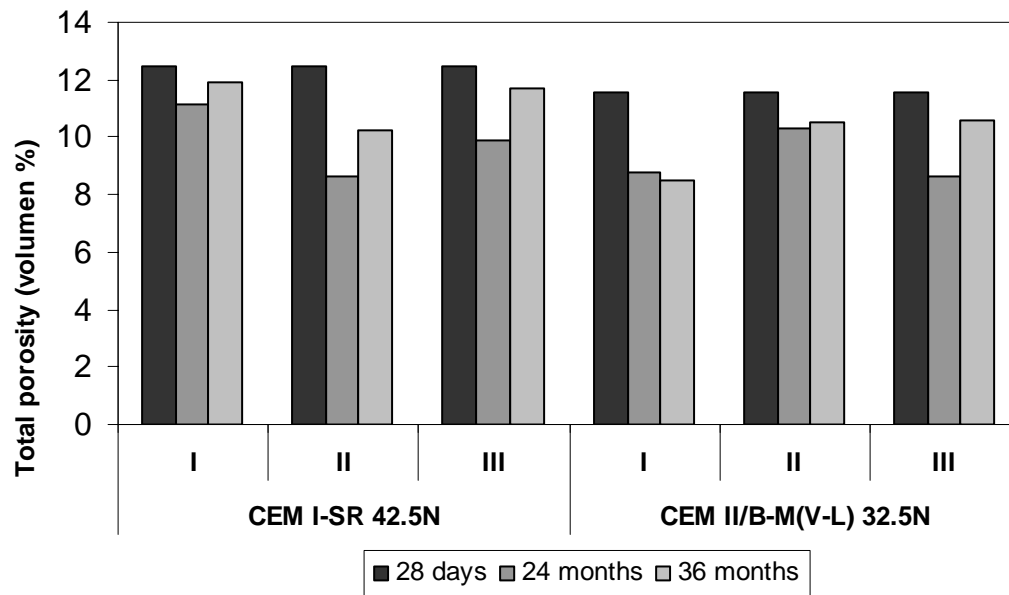


Figure 5. Total porosity by mercury intrusion porosimetry expressed in volume percentage.

Total porosity and compressive strength values in specimens exposed to slurry attack an inverse relationship, which is in line with findings reported by other authors [16-18].

Figures 6 and 7 show pore size distribution for cements CEM I and CEM II, respectively, after 28 days of curing and 3, 24 and 36 months in a natural environment.

After 28 days of curing, the porosity results for the two cements studied were similar, because at first the fly ash behaves like an inert material [19]. The variations in distribution in a natural medium differed widely, however. In cement CEM I, the 24-month findings showed a clear shift toward larger radii, with a reduction in porosity. The mean pore radius rose slightly in cement CEM II, in conjunction with a decline in total porosity.

These findings are consistent with leaching processes associated, in the case of CEM II, with a reduction in total porosity due to the pozzolanic reaction generated by the fly ash. In principle, no other mechanism appears to be involved [8].

Figures 8 and 9 show pore size distribution for cements CEM I and CEM II, respectively, after 28 days of curing and 3, 24 and 36 months in an aerobic environment.

In this environment, the pore size distribution was similar for the two cement mortars studied. Total porosity tended downward, with no significant change in pore size distribution. This trend reached a nadir at 24 months and in both cements began to revert after 36 months.

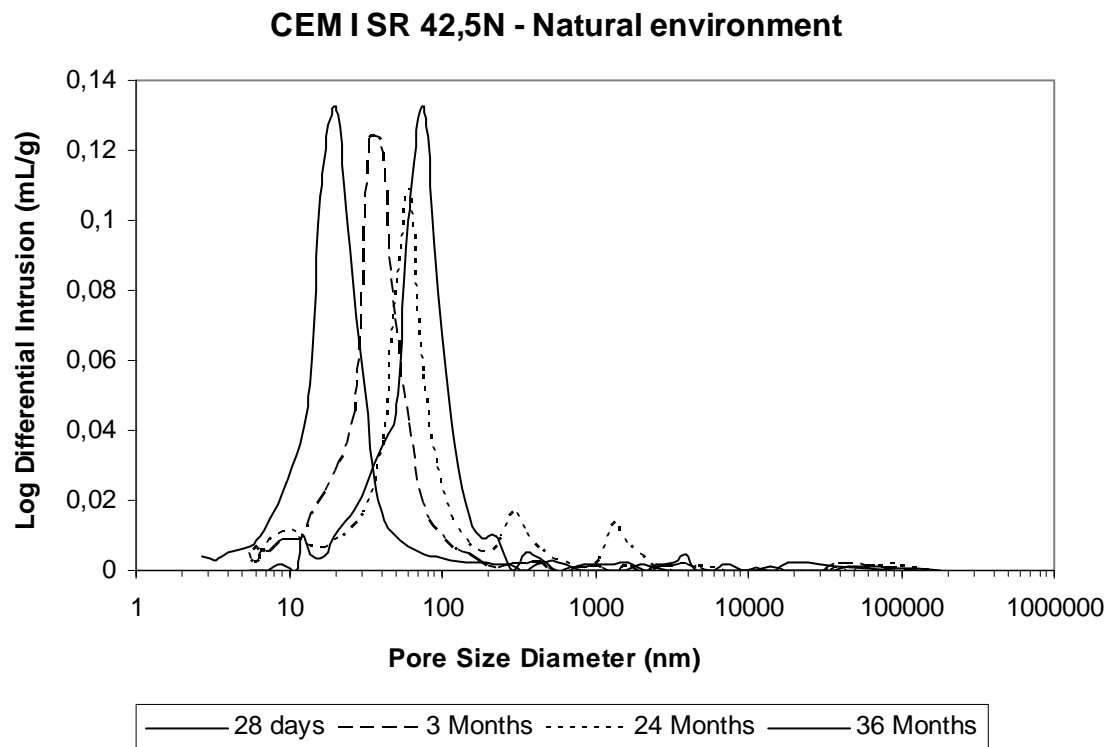


Figure 6. Pore-size distribution for the CEM I cement in the natural environment.

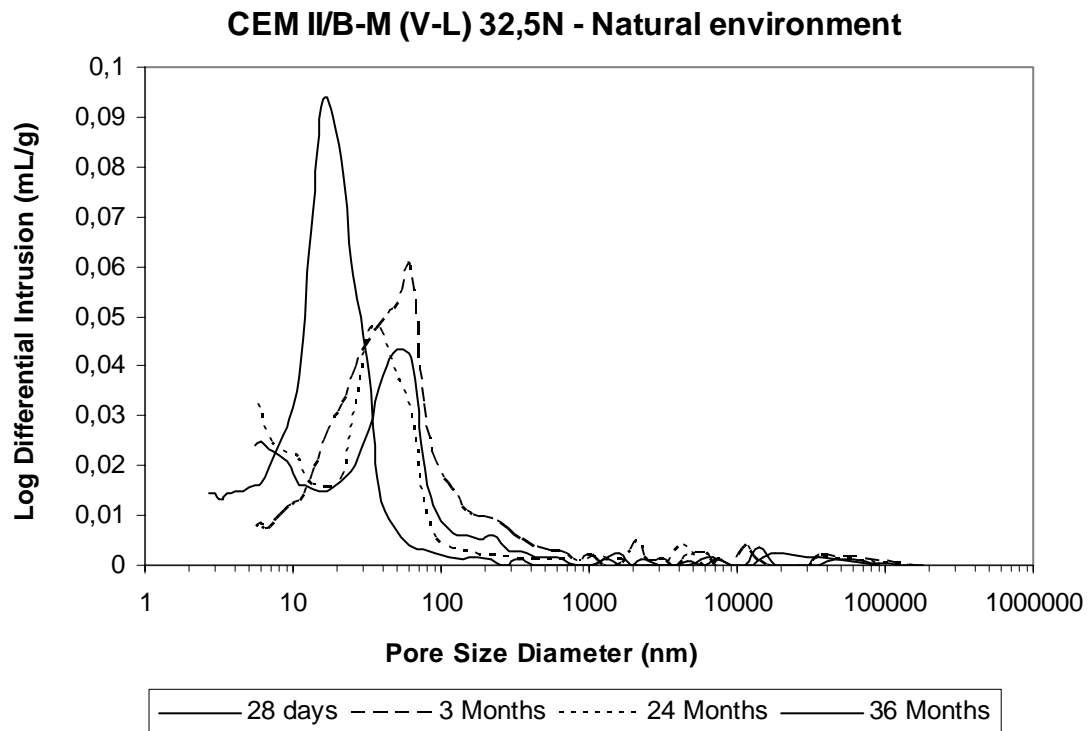


Figure 7. Pore-size distribution for the CEM II cement in the natural environment.

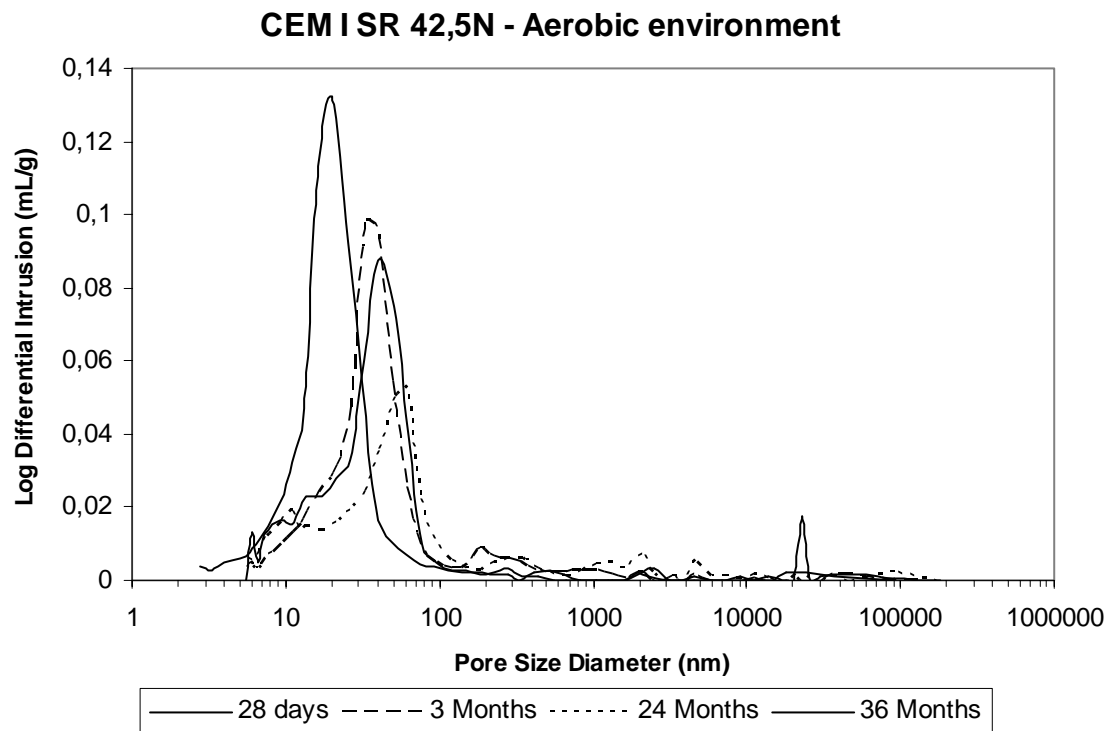


Figure 8. Pore-size distribution for the CEM I cement in the aerobic environment.

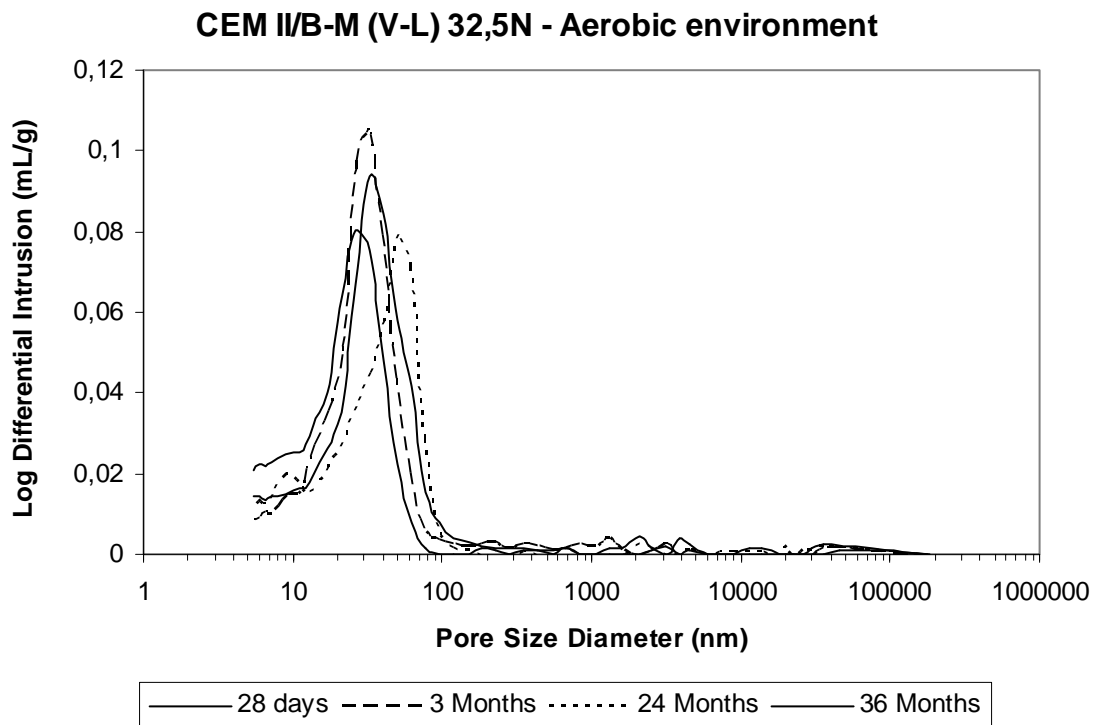


Figure 9. Pore-size distribution for the CEM II cement in the aerobic environment.

Likewise in both cements, the shift toward smaller pore sizes was less perceptible than in the natural medium.

These changes in pore size distribution illustrate the alterations taking place in the specimens. The natural environment clearly prompted leaching in both cements and an increase in the mean radius, more significantly in CEM I.

Pore size underwent less change in submerged environments, with a reduction in pore radius recorded for CEM II. That decline was consistent with the presence of fly ash in its composition [20].

4 Conclusions

Since the strength studies showed that the load capacity attained by the two cements was similar after 36 months. The more expensive 42.5 sulphate-resistant cement is not justified to use. After 36 months, both cements showed signs of declining strength in submerged environments. Moreover, both had shown increased strength in submerged environments at earlier ages, presumably due to intensified hydration. These increases disappeared altogether after 36 months.

The following conclusions may be drawn from the above findings:

- Since the 36-month load capacity of the cements studied was similar, the use of a higher strength, sulphate-resistant cement is not justified. Lower strength class cement with fly ash additions performed equally well, at a lower price.
- In submerged environments, the two cements exhibited greater strength at the various ages. In such media, the decline recorded after 36 months was never smaller than the variation observed in the natural environment.
- The increase in the mean pore size observed in the natural environment did not lead to lower strength in the test period. The changes in pore size distribution and mean pore size values were scanty significant in submerged environments.
- Although up to the age of 24 months, porosity declined in submerged environments, after that age and up to 36 months, this parameter was observed to increase. This may indicate the onset of mortar degradation. In CEM II, where the changes were less significant, the degradation process could be expected to proceed at a slower pace.
- The slurry used can be regarded to be an aggressive agent for cement mortars after 24 months of exposure, in both aerobic and anaerobic conditions.

Acknowledgements

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